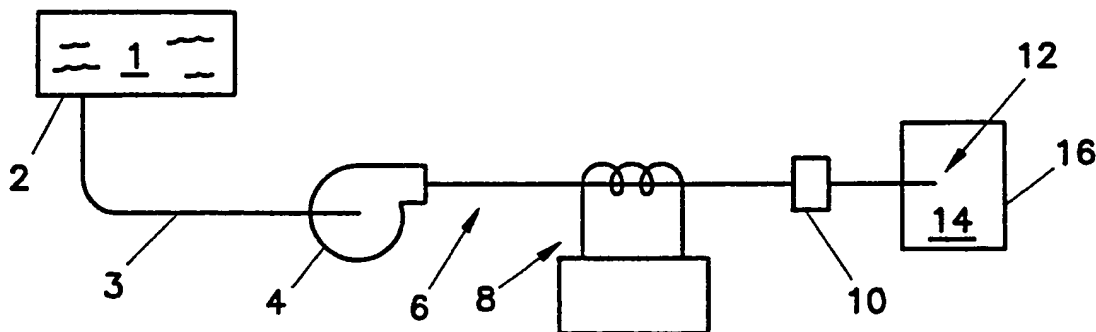




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C01B 13/36, C01G 1/12, 49/06 C01G 25/02	A1	(11) International Publication Number: WO 94/01361 (43) International Publication Date: 20 January 1994 (20.01.94)
(21) International Application Number: PCT/US93/06415 (22) International Filing Date: 7 July 1993 (27.07.93) (30) Priority data: 07/911,842 10 July 1992 (10.07.92) US (71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/ US]; Pacific Northwest Laboratories, Intellectual Property Services, 902 Battelle Boulevard, P.O. Box 999, Richland, WA 99352 (US). (72) Inventors: MATSON, Dean, W. ; 4104 West 17th Avenue, Kennewick, WA 99337 (US). FULTON, John, L. ; 1809 Hunt Avenue, Richland, WA 99352 (US). LINEHAN, John, C. ; 121 Orchard Way, Richland, WA 99352 (US).		(74) Agent: MAY, Stephen, R.; Battelle Memorial Institute, Pa- cific Northwest Laboratories, Intellectual Property Ser- vices, 902 Battelle Boulevard, P.O. Box 999, Richland, WA 99352 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>

(54) Title: METHOD AND APPARATUS FOR MAKING NANOMETER SIZED PARTICLES

**(57) Abstract**

The invention is an improvement to hydrothermal methods wherein a solution of precursor and solvent continuously flow through a heated vessel and chemically react to nucleate particle precipitates, then flow into a cooled region for recovery of the particles. By using continuous flow, the amount of time that the solution is at selected conditions of temperature and pressure are more precisely controllable and shorter (less than one minute and more frequently on the order of seconds) compared to a batch process. Flow of solution into the cooled region results in nearly instantaneous cooling of the solution. Use of the continuous process of the present invention permits production of materials not producible with existing continuous processes at a rate from about tens of grams of particles per hour to about several kilograms of particles per hour. In addition, particle size distributions are narrow and controllable.

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**METHOD AND APPARATUS FOR MAKING
NANOMETER SIZED PARTICLES**

5

FIELD OF THE INVENTION

The present invention relates generally to a method and apparatus for making nanometer-sized particles. More specifically, the method is making a solution of a soluble precursor in a liquid solvent, then continuously flowing
10 the solution through a heated vessel and forming particles within the heated vessel, then recovering the particles by quenching the solution in a cooled region.

BACKGROUND OF THE INVENTION

Particles ranging in size from 1 nm (nanometer, 10^{-9}
15 meter) to more than 100 nm exhibit unique and useful surface and interface properties because they contain a high proportion of surface-to-bulk atoms. Uses of these particles include but are not limited to heterogenous catalysts, ceramic materials fabrication, intermetallics,
20 electronics semiconductor fabrication, magnetic recording media, and superconductors.

Production of nanometer-sized particles is currently accomplished in a variety of ways, including gas phase condensation, laser synthesis processes, freeze drying
25 methods, flame or plasma torch reactions, vacuum synthesis methods utilizing sputtering, laser ablation, liquid metal ion sources, reverse micelle solutions, solidification

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from the liquid state, and hydrothermal methods. These techniques are typically batch techniques and have limited particle production rate (on the order of gram quantities or less per day) and limited overall production quantity. Additionally, relatively wide ranges of particle sizes are produced by these techniques.

It is a long felt need in the art of nanometer-sized particle production to be able to produce larger quantities at faster rates and to be able to control product particle size distribution in order to improve performance and cost of products including but not limited to those enumerated above.

Because the present invention is most related to hydrothermal methods, they are further summarized herein. Hydrothermal methods utilize conditions of elevated temperatures and/or elevated pressures wherein particles are formed by nucleation and grown under these conditions to produce powder products.

Conventional hydrothermal methods begin with making a batch of a solution of a soluble precursor in a liquid solvent. The batch is placed in a vessel. Particles are formed by chemical reactions resulting in nucleation forming precipitates within the vessel. Reactions may be enhanced by heating or pressurization, or both. Heating includes a "ramped" heating stage to bring the solution to a desired temperature. For aqueous solutions, the temperatures are generally in the range from about 90°C to greater than 500°C. The "ramped" heating stage is followed by a holding stage wherein the solution is maintained at the desired temperature, then cooled. Time for ramping and holding typically varies from hours to days depending upon the type of solution and the desired product. Termination of particle growth is achieved by stopping the reaction, generally by cooling the heated solution. Remaining liquid is decanted and the particles dried and recovered.

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Particle sizes are a result of concentrations of reactants, the amount of time that the reactants are in contact, and the temperature and pressure of the reactant solution. Using current methods, it is difficult to
5 control the amount of time reactants are in contact at given conditions of temperature and pressure because of large total heat capacity of vessels and equipment.

Particles are made of materials including but not limited to oxides and hydroxides by hydrolysis or
10 oxidation reactions in aqueous solvent systems, and metals in non-aqueous systems; for example, organometallic species, as well as non-oxide ceramic particles formed by reaction of a precursor with a solvent. More specifically, particle products include but are not limited to
15 iron oxide, titanium oxide, nickel oxide, zirconium oxide, aluminum oxide and silicon oxide. Precursor solutions from which particles are made include but are not limited to aqueous nitrate solutions, sulfate solutions, and oxalate solutions. For example, iron oxide particles may
20 be made from $\text{Fe}(\text{NO}_3)_3$ or $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$.

Further operational details of hydrothermal methods may be found in Hydrothermal Synthesis of Advanced Ceramic Powders, William J. Dawson, Ceram. Bull., 67, 1988 pp. 1673-1677, and in The Role of Hydrothermal Synthesis in
25 Preparative Chemistry, Albert Rabenau, Agnew. Chem. Int. Ed. Engl., 24, 1985, pp. 1026-1040.

Another example of hydrothermal methods is found in the patent 4,734,451 issued on March 29, 1988 to RD Smith, entitled SUPERCRITICAL FLUID MOLECULAR SPRAY THIN FILMS
30 AND FINE POWDERS. Smith teaches the formation of fine powders by dissolving a solid material into a supercritical fluid solution and rapidly expanding the solution through a short orifice into a region of low pressure thereby nucleating and forming particles in the region of
35 low pressure. This process differs from the ones described above inasmuch as it is a continuous process and

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there is no chemical reaction between the solid material and the supercritical fluid solution. While the Smith process is useful for soluble polymers, organic compounds, and many inorganic compounds, it is not useful for insoluble or substantially insoluble ceramic materials, metal oxides, and other above mentioned substantially insoluble materials. In addition to requiring dissolution of the particle forming compound, the Smith process requires carrier solutions which have no liquid droplet formation upon expansion to low pressure, whereas the present invention does not require this limitation.

SUMMARY OF THE INVENTION

The invention is an improvement to hydrothermal methods wherein a solution of precursor and solvent continuously flow through a heated vessel and chemically react to nucleate particle precipitates within the vessel, then flow into a cooled region for recovery of the particles. By using continuous flow, the amount of time that the solution is at selected conditions of temperature and pressure are more precisely controllable and shorter (less than one minute and more frequently on the order of seconds) compared to a batch process. Flow of solution into the cooled region results in nearly instantaneous cooling of the solution and terminate particle growth.

Use of the continuous process of the present invention permits production of materials not producible with existing continuous processes at a much faster rate compared to existing batch methods. Production rates of the present invention are from about tens of grams of particles per hour to about several kilograms of particles per hour. In addition, particle size distributions are narrower compared to batch methods.

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The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with
5 further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

10 FIG. 1 is a schematic of an embodiment of the present invention.

FIG. 2 is a schematic of a second embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

15 The invention is an improvement to hydrothermal methods wherein a solution of precursor and solvent continuously flow through a heated vessel and the solute chemically reacts to nucleate particle precipitates, then flows into a cooled region for recovery of the particles.

20 An apparatus for carrying out the present invention is shown in FIG. 1. Solution (1) within reservoir (2) flows into a first tube (3) and is pressurized by a pump (4). Pressurized solution flows into a reaction vessel (6) that may be any type of closed and pressurizeable
25 continuous flow vessel having an inlet and outlet, but is preferably a tube. The reaction vessel (6) is heated by a heater (8). Pressure may be maintained within the reaction vessel (6) by any pressure control means, but preferably with a flow restrictor (10) located downstream
30 of both the pump (4) and the heater (8). The heated solution is cooled by ejection from the end (12) of the

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reaction vessel (6) into a chamber (14) having walls (16) that are cooled. The heated solution is rapidly cooled within the chamber (14). Particles and reacted solution accumulate within the chamber (14). Particles are
5 recovered by any method including but not limited to settling, filtering, or centrifugation. Remaining liquid is decanted and the particles dried under flowing nitrogen or air.

The heater (8) may be of any type including but not
10 limited to electrical resistance heaters, induction heaters, microwave heaters, fuel fired heaters, and steam coils. It is preferred that the heater be the tube itself resistively heated with electricity.

The flow restrictor (10) may be of any type
15 including but not limited to an adjustable valve, or a non-adjustable orifice such as a nozzle or lengths of small diameter tubing.

The walls (16) may be cooled by any means including but not limited to refrigeration coils, water/ice bath,
20 liquid nitrogen, and dry ice.

A second embodiment of an apparatus according to the present invention is shown in FIG. 2. Instead of an open chamber (14) for cooling and particle collection, a section of the reaction vessel (6) is cooled by a cooling
25 means (21) downstream from the heater (8). Upon exiting the cooled section of reaction vessel (6), the solution (1) enters a filter means (22) wherein particles are collected while remaining liquid flows through the flow restrictor (10) to a catch basin (24).

30 The cooling means (21) may be any means including but not limited to low temperature baths, including water and ice baths, and dry ice, as well as refrigeration cooling coils.

Although it is preferred to use a pump (4), it is
35 not necessary since the solution (1) is pressurizeable by any means including but not limited to mechanical pistons

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with weights on them, overpressure of a gas, and hydraulic head.

The first two embodiments disclose a reservoir (2) holding a solution (1). Depending upon the desired product and the precursors and solvents necessary to obtain the product, the reaction vessel tube (3) may be provided with multiple ports for staged injection of precursors and solvents. The tube (3) itself may be a concentric tube having an inner and outer tube with an annular space therebetween.

Co-processing of precursors, solvents, or reagents having different reaction temperatures may be accomplished with a multi-port or concentric tube reaction vessel. The heated region of the reaction vessel tube may be controlled to exhibit a temperature variation along its length wherein various compounds may be added into an appropriate temperature zone.

In operation, particle size is determined by many factors including temperature, pressure, type of flow restrictor, and concentration and type of precursor in the solution. Flow rate of solution to achieve a particle production rate depends upon the same factors recited above and may vary over a wide range. For operational convenience, flow rates and tube lengths are selected to provide a residence time of solution (1) within the vessel (3) of less than one minute, and preferably about 2 to 3 seconds. The temperature and pressure of the solution within the vessel may also vary widely depending upon the type of solution and the size of particles desired. Temperatures may range from about 25°C (ambient) to greater than 500°C, but are preferably from about 200°C to about 400°C. Pressures are sufficient to prevent substantial vaporization of the solution thereby maintaining the solution substantially in the liquid phase. The terms "substantial" and "substantially" are used because it is recognized that vaporization may not be completely

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avoided. Furthermore, some vaporization of solution is not harmful to the process of the present invention.

The process of the present invention is not limited to the type of chemical reaction occurring within the reaction vessel. It is preferred, however, that the reaction take place within the reaction vessel and not within the inlet reservoir or the outlet. The chemical reaction may be an interaction of the precursor with the solvent at elevated temperature conditions, for example oxide formation. The chemical reaction may be a thermal breakdown of the precursor into an insoluble form, for example formation of iron particles from an iron pentacarbonyl/carbon dioxide solution. The chemical reaction may be thermal decomposition of an additional reactant, for example addition of urea decomposing into ammonia in a solution of iron nitrate and forming iron hydroxide particles.

The apparatus and method or process of the present invention can accommodate any combination of precursor and solvent provided that the precursor is soluble in the solute. Solvents may be selected from inorganic and organic liquids. Inorganic liquids include but are not limited to water (aqueous solvent) and ammonia. Organic liquids that may be used as solvents in the present invention include but are not limited to carbon dioxide, hydrocarbons, halogenated hydrocarbons, and alcohols. Precursors that are aqueous soluble include but are not limited to ferric or ferrous salt, for example, ferric halide, ferric sulfate, ferric (periodic chart column 1A element) sulfate; oxalates of potassium, sodium, ammonium, lithium, oxotitanium, zirconium, hafnium, and citrates of zirconium and titanium. Precursors that are soluble in carbon dioxide, especially supercritical carbon dioxide, include but are not limited to $\text{Fe}(\text{CO})_5$ and $\text{Mo}(\text{CO})_6$.

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An additional solute may be oxidizing like urea or reducing like hydrazine, hydrogen gas or sodium borohydride.

EXAMPLE 1

5 An experiment was performed to produce particles according to the method of the present invention using an apparatus according to FIG. 1. An aqueous solution of iron nitrate ($0.1M \text{ Fe}(\text{NO}_3)_3$) was pressurized with a reciprocating pump (4) to a pressure of about 510 Bar
10 (7500 psi) and transported through a reaction vessel (6). The reaction vessel (6) was 316 stainless steel tubing having an outside diameter of 0.32 cm, a wall thickness of 0.09 cm, and a length of 90 cm. The reaction vessel (6) was heated by resistive electrical heating. The solution
15 had a flow rate of about 50 cc/min. The tube temperature was held constant for each run and several runs having temperatures ranging from about 225°C to about 400°C were made.

The flow restrictor (10) was constructed of a short
20 length (length less than about 2.5 cm) of capillary tubing having an inside diameter from about 60 micrometers to about 100 micrometers.

The heated solution was ejected into a flask immersed in a water/ice bath.

25 Phase identification and size of the particles was performed using X-ray particle diffraction. Diffraction patterns were obtained using a Philips X-ray diffractometer with a copper source operated at 40 kV and 25 mA. Particle size estimates were made by calculations based
30 upon the Scherrer formula as may be found in the book entitled ELEMENTS OF X-RAY DIFFRACTION, 2d edition, by BD Cullity, published by Addison Wesley, Reading, Mass. in 1978. A correction for instrument broadening was made to the Scherrer formula.

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Particle size and particle size distribution were obtained using transmission electron microscopy micrographs of particles deposited upon 3 mm carbon coated grids. The particles were micrographed in a Philips
5 EM400T electron microscope operated at 120 keV. Particle size distributions were also obtained using variable temperature Mossbauer spectroscopy as described in the article entitled MOSSBAUER EFFECT STUDIES OF SURFACE IONS OF ULTRAFINE ALPHA-IRON(III) OXIDE PARTICLES, by AM Van
10 der Kraan, published in Phys. Stat. Sol. A, Vol. 18, pp 215, 226 in 1973.

Surface area was obtained by a nitrogen absorption method using a micrometrics ASAP 2000 instrument for further confirmation of the particle size measurements.

15 Results are shown in Table 1. For the identified sample numbers, processing parameters of temperature and pressure are shown. Results of yield, material phase, and particle size are also shown. Particle diameters are reported for three independent measurements along with
20 confirmatory surface area measurements. From Table 1, one can see that particle sizes are larger for higher processing temperature. One also sees that the particle size range is narrow, showing size range variations of from 8 to 50 nm.

25 EXAMPLE 2

An experiment was performed to produce particles according to the method and using the apparatus set forth in Example 1. However, in this experiment, an aqueous solution of potassium bis(oxalato)exotitanate (IV) (0.1M
30 $K_2TiO(C_2O_4)_2$) was used. The solution had a flow rate of about 50 cc/min, and was heated in a reaction vessel tube (6) made of Hastelloy C-276.

Results are shown in Table 2. From Table 2, one can see that the particle size range is narrow, showing range
35 variations of 5 nm.

TABLE 1. Iron-Oxide Powders Produced From $\text{Fe}(\text{NO}_3)_3$

Sample #	Processing Parameters		Phase	Crystallite Diameter, nm			Surface Area, m^2/g
	Temperature, °C	Pressure, MPa		XRD	TEM	Mossbauer	
654-44-1	225	40-55	Goethite	< < 10	2-10	100% < 8.5	212
654-43-1	225	48-55	Goethite	< < 10	2-10	100% < 8.5	112
062-29-2	300	40-55	Hematite	11	10-20	56% > 8.5	167
654-45-1	300	40-55	Hematite	16	--	--	202
062-29-1	400	40-55	Hematite	23	20-70	--	--
654-45-2	400	40-55	Hematite	28	--	90% > 8.5	--
399-92-6	200	40-55	Unknown	< < 10	--	100% < 8.5	183

TABLE 2. Iron-Oxide Powders Produced From $K_2TiO(C_2O_4)_2$

Processing Parameters		Phase	Crystallite Diameter, nm			Surface Area, m ² /g
Temperature, °C	Pressure, MPa		XRD	TEM	Mossbauer	
200	40-55	TiO ₂ (Anatase)	3.1	--	--	--
250	40-55	TiO ₂ (Anatase)	4.2	--	--	--
300	40-55	TiO ₂ (Anatase)	4.1	2-7	--	134

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EXAMPLE 3

Another experiment was conducted according to the method and using the apparatus of Example 1. In this experiment, a solution of aluminum nitrate (0.1 M) $\text{Al}(\text{NO}_3)_3$ was used. The solution was processed at a temperature of about 400°C and produced very few particles.

Urea ($\text{CO}(\text{NH}_2)_2$) was added to the solution and particles were made at temperatures from between about 200°C to about 300°C .

EXAMPLE 4

Other experiments conducted according to the method and apparatus of Example 1 but using different combinations of solutions and precursors. The combinations and resulting particle or powder products are summarized in Table 3.

The results shown in Table 3 are demonstrative of the variety of particles that may be produced with the present invention.

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

TABLE 3. Other Powders Produced

Precursor	Solvent	Temperature, °C	Pressure, MPa	Powder Material	Crystallite Diameter, nm		Surface Area, m ² /g
					XRD	TEM	
FeCO ₅	CO ₂	350	17.2	Alpha-Fe	5.4	--	--
Ni(NO ₃) ₂	water	450	55	NiO ₂	127	--	--
Zirconium (IV) Citrate Ammonium Complex	water	350	40-55	ZrO ₂ (Cubic)	3.5	--	--
Zirconium (IV) Citrate Ammonium Complex	water	400	40-55	ZrO ₂ (Cubic)	3.5	--	--

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CLAIMS

We claim:

1. A method of making nanometer-sized particles, comprising the steps of making a solution of a soluble precursor in a liquid solvent, pressurizing and heating said solution and initiating chemical reactions nucleating and forming substantially insoluble solid particles then quenching said heated solution and arresting growth of said solid particles, wherein the improvement comprises:
 - 10 flowing said solution through said vessel in a continuous manner.
2. A method as recited in claim 1, wherein said solvent is water.
- 15 3. A method as recited in claim 1, wherein said solvent is an organic liquid.
4. A method as recited in claim 1, wherein said solvent is a supercritical fluid.
5. A method as recited in claim 4, wherein said
20 supercritical fluid is carbon dioxide.
6. A method as recited in claim 1, wherein said precursor is selected from the group of ferrous salts, metallic oxalates, metallic citrates, and metallic carbonyls.
- 25 7. A method as recited in claim 1, wherein said solid particles are selected from the group of metals, metal oxides, intermetallics, and metal sulfides.

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8. A powder having particles made by the method of claim 1.

9. A method as recited in claim 1, wherein said chemical reaction is an interaction of said precursor with
5 said solvent.

10. A method as recited in claim 9, wherein said precursor is a metal salt hydrolyzed to a metal hydroxide.

11. A method as recited in claim 9, wherein said precursor is a metal salt oxidized to a metal oxide.

10 12. A method as recited in claim 1, wherein said chemical reaction is thermal breakdown of said precursor.

13. A method as recited in claim 12, wherein said precursor is a metal carbonyl yielding metal.

14. A method as recited in claim 1, wherein an
15 additional solute is added to said solution.

15. A method as recited in claim 14, wherein said chemical reaction is thermal decomposition of said additional solute.

16. A method as recited in claim 1, wherein said
20 particles have absolute sizes from 1 nm to 150 nanometers with size distribution ranges varying from 8 to 50 nanometers.

17. A method as recited in claim 1, wherein said particles are produced at a rate from about 10 g/hr to
25 about 2 kg/hr.

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18. An apparatus for making nanometer-sized particles comprising a reaction vessel for receiving a solution of soluble precursor in a liquid solvent, said reaction vessel pressurizeable and heatable for initiating
5 chemical reactions for nucleating and forming solid particles, wherein the improvement comprises:

(a) said reaction vessel is a continuous flow vessel having an inlet and outlet, and

(b) a means for cooling said solution downstream
10 of a heating means.

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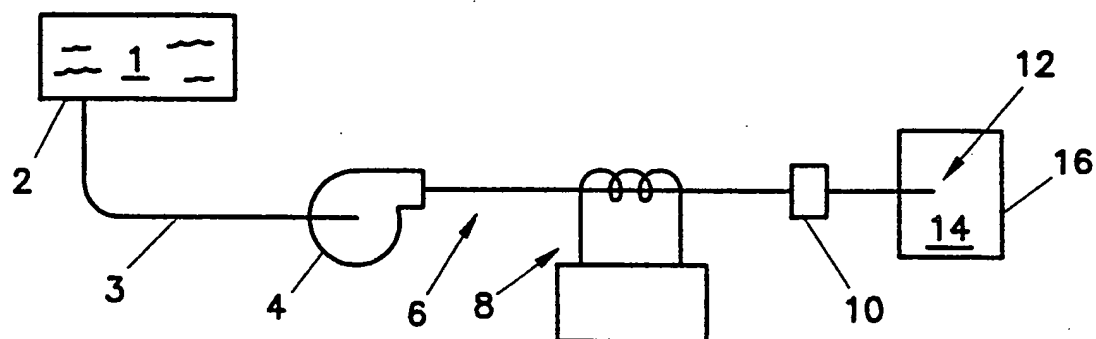


FIGURE 1

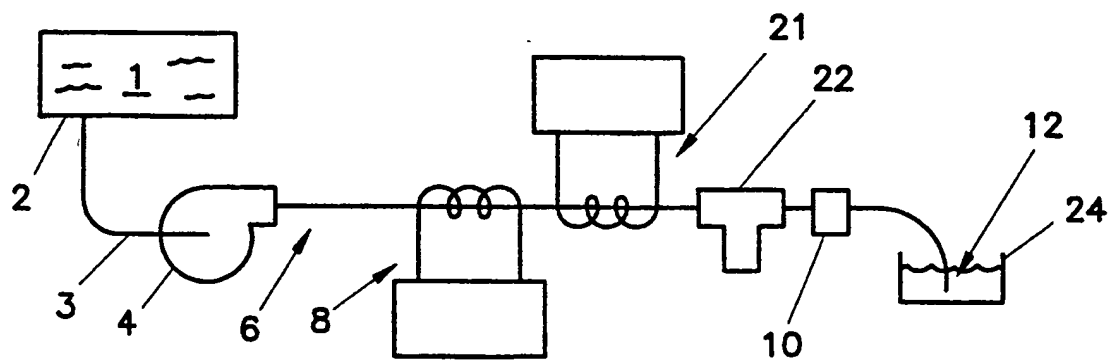


FIGURE 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/06415

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C01B13/36 C01G1/12 C01G49/06 C01G25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C01B C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF THE AMERICAN CERAMIC SOCIETY. vol. 75, no. 4, April 1992, COLUMBUS US pages 1019 - 1022 TADAFUMI ADSCHIRI 'RAPID AND CONTINUOUS HYDROTHERMAL CRYSTALLISATION OF METAL OXIDE PARTICLES IN SUPERCRITICAL WATER' see the whole document ---	1,2,4, 6-10, 16-18
X	WO,A,89 03365 (ALLIED-SIGNAL INC) 20 April 1989 see the whole document ---	1,2,9,10
X	E.M.ADKINS 'LIGHT METALS 1983' March 1983, METALLURGICAL SOCIETY OF AIME , UNITED ARAB EMIRATES see page 1145 - page 1158 ---	1
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

18 November 1993

Date of mailing of the international search report

07.12.93

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/06415

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN & JP,A,55 136 130 (YAMAZAKI NAKAMICHI) 23 October 1980 see abstract</p> <p>-----</p>	1,18

Information on patent family members

PCT/US 93/06415

Form PCT/ISA/210 (parent family annex) (July 1992)